

Audit of Data Quality Report

Data Associated with Pavillion Ground Water Investigation Phase V April 2012 Sampling Event

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July 18, 2012
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Phase V April 2012 Sampling Event

ADQ performed by Neptune and Company, Inc.

1. INTRODUCTION:

This Audit of Data Quality (ADQ) was performed per the NRMRL SOP, *Performing Audits of Data Quality (ADQs)*, to verify that requirements of the Quality Assurance Project Plan (QAPP) were properly implemented for the analysis of samples submitted to laboratories identified in the QAPP associated with this project. The associated QAPP for this case study was entitled *Ground-Water Investigation in Pavillion, Wyoming (QA ID G-14478, Revision 6, February 17, 2012)*.

2. ADQ APPROACH:

Complete data packages were provided to the auditors for the Pavillion Wyoming April 2012 sampling event. A complete data package consists of the following: sample information, method information, data summary, laboratory reports, raw data including QC results, and data qualifiers. The QAPP was used to identify data quality indicator requirements and goals, and a checklist was prepared based on the types of data collected. Metals data were reviewed using revised acceptance criteria dated May 22, 2012.

The data packages were reviewed against the checklist by tracing a representative set of the data in detail from raw data and instrument readouts through data transcription or transference through data manipulation (either manually or electronically by commercial or customized software) through data reduction to summary data, data calculations, and final reported data. All calibration and QA/QC data were reviewed for all data packages identified in Table 1. Auditors also reviewed the final data summary (Excel Spreadsheet, "*Pavillion Apr2012 QA Summary v0.xlsx*") and "*Pavillion Apr2012 QA Summary v1.xlsx*" to determine if data had been accurately transcribed from lab summary reports and appropriately qualified based on lab and field QC results.

The critical analytes, as identified in the QAPP (Table 9), are Gasoline Range Organics (GRO); Diesel Range Organics (DRO); Semivolatile Organic Compounds (SVOCs); Volatile Organic Compounds (VOCs) of ethanol, isopropyl alcohol, tert-butyl alcohol, naphthalene, benzene, toluene, ethylbenzene, and xylene; major cation potassium, major anion chloride. Note, the VOC analysis performed by Region 8 does not include ethanol, isopropyl alcohol, or tert-butyl alcohol.

Also included in this ADQ are the following analytes: dissolved inorganic and organic carbon;

dissolved gases by GC; stable oxygen and hydrogen isotopes of water; low molecular weight acids by HPLC; stable carbon isotope ratio of dissolved inorganic carbon, stable carbon and hydrogen isotope ratios of dissolved methane; tritium; MBAS (methylene blue active substance), glycols; ethoxylated alcohols and alkylphenols; acrylamide; methanol, ethylene glycol, and propylene glycol.

Table 1 below summarizes the samples and laboratory analyses reviewed as part of this Version 2 ADQ Report. Future reports will incorporate the remaining analytical suites discussed above that are not included in Table 1 below.

Sample Identification	Laboratory	Analyses (all samples)
PGDW05-0412	EPA, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center Shaw Lab at Ada, OK	Metals and major cations (calcium, magnesium, potassium, sodium, arsenic, selenium, uranium), headspace analysis of VOC (critical), stable oxygen and hydrogen isotopes of water, low molecular weight acids by HPLC, dissolved gases of methane, ethane, propane and n-butane.
PGDW20-0412		
PGDW20d-0412		
PGDW23-0412		
PGDW30-0412		
PGDW50-0412		
PGPW02-0412		
EPAMW02-0412-1		
EPAMW02-0412-2	TestAmerica Inc, Savannah Georgia	Methylene Blue Active Substances (MBAS)
EPAMW01-0412		
EPAMW01d-0412		
EPAMW01-0412-2		
EPAMW01-0412-3		
EPAMW01-0412-4	Isotech Laboratories, Champaign Illinois	Stable carbon isotope ratio of DIC, stable carbon and hydrogen isotope ratios of dissolved methane, tritium
EPAMW01-0412-5		
EPAMW01-0412-6		
EPAMW01-0412-7		
EPAMW01-0412-8		
	EPA, Region VIII Golden Colorado	VOCs, SVOCs, GRO, DRO

EPAMW01-0412-9		
EPAMW01-0412-10		
Associated Field Blanks, Equipment Blanks, and Trip Blanks	EPA, Region III, Environmental Science Center at Ft. Meade, MD	Glycols
	RSKERC General Parameters Lab, Ada, OK	DOC, DIC, anions of chloride and sulfate
	ALS Laboratories	methanol, ethylene glycol, propylene glycol

Table 1. Samples and associated laboratories under this ADQ Report.

3. ADQ REPORT CONTENT:

This ADQ report includes the audit approach, the audit results, and the completed ADQ checklist.

4. ADQ RESULTS:

ADQ Definitions

To assist in the interpretation of this ADQ report, the following definitions are provided:

Deficiency – an identified deviation from project QA/QC requirements.

Finding – a deficiency that has or may have a significant effect on the quality of the reported results. A corrective action response is required.

Observation – a deficiency that does not have a significant effect on the quality of the reported results. A corrective action response is required.

Additional Comment – an issue that is not a deficiency but may need to be considered to improve or clarify current processes. A corrective action response is not required.

ADQ Summary

The QA/QC requirements specified in the associated QAPP have been met or the data appropriately qualified, with the following exceptions. The completion of appropriate corrective actions will minimize any significant impact to the data summarized for reporting.

Observations

1. **Field and Equipment Blanks, all analyses.** Section 4.1.d of the QAPP indicates that a Field Blank and Equipment blank will be collected on every day of sampling. For all of the analyses reviewed in this ADQ, this requirement was not met. In most cases samples were collected on seven different days, but only 3-4 Field and Equipment (where applicable) Blanks were collected. In addition, the following qualification issues associated with blanks are identified.
 - a. The DOC result for sample PGDW05-0412 should be flagged FB due to the associated Field Blank that is not less than ten times the concentration of this sample. It is noted that the associated Equipment Blank was a non-detect.
 - b. The total selenium values for several samples (PGDW05-0412, PGDW20-0412, PGDW20d-0412) are less than ten times the associated Field Blanks. These samples should be flagged FB. Also, samples, EPAMW01-0412-10, and EPAMW01-0412, and EPAMW01d-0412 are less than ten times the associated Equipment Blank concentration and should be qualified EB.
 - c. The Field Blank and Trip Blanks for dissolved gases. The final summary spreadsheet includes the FB and EB flags for two samples collected on 4/19 and 4/20. It is unclear why these flags have been added since there are no Field or Equipment Blanks for these days.

Recommended Correction Action. (a) In the summary spreadsheet, qualify all results above MDL for which there is not a corresponding FB and or/ EB. Existing qualifiers do not cover this issue, so a new one may be created. The field crews need to be sure that all field QC samples are collected. Each day of sampling a Field Blank and Equipment Blank are to be collected. How this impacts sample data interpretation needs to be addressed in the QAQC write-up. (b) Flag the samples identified above (for DOC and total Se) with “FB” to indicate their values are less than ten times the associated Field Blank value. (c) Remove the FB and EB flags for samples PGDW50-0412 and PGPW02-0412 for dissolved gases unless these samples are associated with Field Blank and Equipment Blank collected on 4/18/2012 based upon field notes.

Corrective Action Performed.

- 2. Metals/major cations via ICP-OES.** As outlined in the table below (checklist item 10), not every element that is reported was included in a continuing calibration check (CCC) standard to bracket all samples. It is noted that the second source standard analyzed prior to the samples did contain all reported elements and was within the acceptance criteria, and when the CCC was analyzed it did meet the acceptance criteria. Therefore there are calibration checks that bracket the samples, but in several instances the beginning check is from the second source, not the CC check standards. These checks indicate the instrument was under control, but that the exact SOP requirements were not met with respect to continuing calibration checks.

The matrix spike samples analyzed by ICP-OES for both the total and the filtered samples for sodium could not be evaluated due to the high sodium concentrations in the samples relative to the spike concentration. For matrix spike samples for filtered samples, one matrix spike for silicon and sulfur could not be evaluated due to the high silicon and sulfur concentrations in the samples relative to the spike concentration. The pre-digestion matrix spike for silver had low recovery, likely due to the lack of HCl acid in the digestion procedure. The post-digestion matrix spike recovery for silver was acceptable.

Recommended Correction Action. (a) The laboratory needs to be instructed to ensure that the analytical runs include CCCs that brackets all samples with all elements that are reported and the matrix spike combinations needs to include all elements. The laboratory should also be instructed to include a LCS that is spiked at the same spiking solution as the samples to allow for evaluations of recovery in instances where sample concentrations are high relative to the spiking concentration. (b) All reported samples need to be flagged J2 due to incomplete CCC frequency for Al, Ag, B, Ba, K, Na, S, Si, and P. (c) Silver needs to be flagged with K2 due to low matrix spike recovery.

Corrective Action Performed.

- 3. Region 3 Glycols: Quality Controls.** Analyte recoveries for continuing calibration verification (CCV) / blank spikes (BS), MRL samples, fell below the percent recovery limits for low BS 5 ppb analyzed on 4-20-21/2012, low BS 5 ppb analyzed on 5/1-2/2012, low BS 10 ppb analyzed on 5/2-3/2012 and low BS 5 ppb analyzed on 5/2-3/2012. For details about the percent recoveries for the affected analytes, please see #11 below in the ADQ checklist table. Note the quantification limit was raised from 5 to 10 ppb for tetraethylene glycol and triethylene glycol based on the low blank spike recoveries at the 5 ppb level.

Matrix Spike 1 and its duplicate (MS1/MSD1) were below the 70-130% limits for all 4 analytes and the RPD was above 25% for 2-butoxy ethanol and triethylene glycol. The laboratory noted these issues and flagged sample results with an "A" in the final report.

Recommended Correction Action. With respect to the CCV/BS issues, non-detect results

for all 4 analytes in samples analyzed on 5/2/2012 and 5/3/12 should be qualified as K2 because of the low recoveries in the BSs (10 and 5 ppb), which are equal to the quantification limit. Therefore, all analytes in the following samples should be qualified as K2 in the final summary spreadsheet: EPAMW01-0412-7 (excluding diethylene glycol due to high detect), EPAMW01-0412-10 (excluding diethylene glycol due to high detect), EPAMW01-0412-4 (excluding diethylene glycol due to high detect) and EPAMW01d-0412 (excluding diethylene glycol due to high detect). The Case Narrative of the lab report recognizes these QC issues and in some cases analytes are J flagged.

MS1/MSD1 were made from source sample PGDW30-0412. All samples analyzed on the same dates as this MS1/MSD1 (4/20-21/2012) should be qualified as K2 (this includes all 4 analytes) due to the low MS recoveries. Affected samples are: Field Blank 1, Equipment Blank 2, PGDW20-0412, PGDW20d-0412, EPAMW02-0412-1, PGDW23-0412, PGDW30-0412, Field Blank 2, Equipment Blank 2, and PGDW05-0412.

Corrective Action Performed.

4. **DOC MDL Value and qualifiers in the Final Summary Spreadsheet.** The Field Blanks and Equipment blanks in the final summary spreadsheet for DOC use a <0.044 value when the analyte was not detected, this is the MDL for DIC not DOC. The DOC result for sample PGDW05-0412 should be flagged FB due to the associated Field Blank that is not less than ten times the concentration of this sample.

Recommended Correction Action. Confirm the correct MDL for DOC and incorporate this in the final data as a <value. Add the FB qualifier to sample PGDW05-0412 in the final summary spreadsheet.

Corrective Action Performed.

5. **Stable oxygen and hydrogen isotope ratios of water.** For the stable hydrogen and oxygen isotopes of water: The replicate injections of the oxygen isotopes for sample PGDW20d-0412 just exceeded the limits. The difference was 0.11 ‰ for $\delta^{18}\text{O}$, above the criteria of $\leq 0.1\text{‰}$. The laboratory report identified this issue and it is believed that rounding is part of the cause to this failure. However, this sample should be qualified in the final summary spreadsheet with a J6.

Recommended Correction Action. Sample PGDW20d-0412 should be qualified in the final summary spreadsheet with a J6.

Corrective Action Performed.

6. **Stable carbon and hydrogen isotope ratios of dissolved methane.** One laboratory

duplicate analysis in Job 17997 of sample EPAMW02-0412-1 exceeded the QAPP Table 10 precision limits of < 3‰ for δDC1 (hydrogen isotopes of methane). The original and duplicate results were -204.6‰ and -208.3‰ respectively with a difference of 3.7‰.

Recommended Correction Action. Sample EPAMW02-0412-1 for stable carbon and hydrogen isotope ratios of dissolved methane should be qualified J6. The laboratory should also re-analyze samples when the precision limits for duplicates exceed 3‰ for δD .

Corrective Action Performed.

7. MBAS: Chain-of-Custody, Initial Calibration Information, Second Source Standard.

- a. For Job Number 680-78755-1, that included only sample PGDW50-0412, the chain-of-custody (COC) date and time was not completed. The COC does include the name of receiver, their signature, and affiliation as TestAmerica. The case narrative in the report indicates the sample was received on 4/20/2012.
- b. The laboratory reports received do not contain initial calibration (ICAL) information. Continuing calibration checks bracket all samples as required. However, there is no information on the ICAL.
- c. The QAPP indicates that a second source standard is to be included with the MBAS analysis, with each new calibration (ICAL), and have recovery of 90-110%. No information on a second source standard was provided by the laboratory. In each set of samples a laboratory control sample (LCS) was analyzed and the recovery of that sample was within these limits (90-110%). Also note the recovery of MBAS in the continuing calibration verification standard that was run prior to and bracketing all samples was not reported.

Recommended Correction Action. (a) It should be noted in the Pavillion report QA section, Appendix B that the receiving laboratory did not document date or time received on the COC, but that the data received as noted in their case narrative. (b) Because no second source standard was provided, all results should be qualified J2.

Corrective Action Performed.

- 8. Reg 8 VOCs: Second Source Standard Checks.** (a) The initial calibrations were not immediately verified by a second source calibration verification (ICV) standard containing all analytes. Instead, a mixture of SRMs was analyzed after the initial calibrations. Because of the lack of complete ICVs, all sample results are qualified as estimated and are suitable for screening purposes only. The final summary spreadsheet does include the J2 qualifier for these results. Based upon the language in the Region 8 laboratory report it would appear that the J8 qualifier should be applied to all VOC values in the final summary spreadsheet, to indicate these are suitable for screening purposes only. (b) Also, sample EPAMW02-0412-2

was diluted 20x but the QLs were not adjusted to account for this factor.

Recommended Correction Action. (a) It is recommended that the final summary spreadsheet include the J8 qualifier for all VOC analytes, all samples. (b) For sample EPAMW02-0412-2 adjust the QLs for the 20x dilution.

Corrective Action Performed.

9. **SVOC Qualifiers.** (a) For compound 2,4-dimethylphenol, all flags associated with the samples that did not detect this compound should be U1 (to match all other analytes) in the final summary spreadsheet. (b). The final summary spreadsheet also needs to use the K qualifier for matrix spike related flags, in place of the current J flags for the compounds and samples noted below.

Recommended Correction Action. (a) Apply the U1 flag in place of the U flag for 2,4-dimethylphenol.

(b) The following revisions to the final summary spreadsheet are necessary:

For sample EPAMW02-0412-1, apply the K2 for analytes bis (2-ethylhexyl) phthalate, chrysene, and terpinol.

For sample EPAMW01-0412, apply the K2 for adamantane and the K1 for phenol

Corrective Action Performed.

10. **GRO.** (a) Two samples were found to be above the pH value of 2 when they arrived at the laboratory: PGDW50-0412 (1204003-18) at pH of 7, and Equipment Blank 4 (1204003-23) at a pH of 5. Sample PGDW50-0412 has been properly qualified in the laboratory report and final summary spreadsheet. However, the final summary spreadsheet needs to include the J9 flag for the Equipment Blank 4. Equipment Blank 4 was analyzed within seven days of collection, meeting the holding time requirement for an unpreserved sample. (b). Sample EPAMW02-0412-2 was analyzed at a 10X dilution for gasoline TPH. The “D(10)” flag should be added to the final summary spreadsheet.

Recommended Correction Action. (a) Qualify Equipment Blank 4 with the J9 flag. Remind the sampling crew to double check the pH value of the samples in the field after they have been acidified to ensure they reach the proper preservation range. (b) Add the “D(10)” flag to the GRO value for sample EPAMW02-0412-2.

Corrective Action Performed.

11. **Low MW Organic Acids.** (a) The lab IDs appear to be wrong in the lab report for PGDW05-0412 (lab ID should be 6511-04, not 6507-4) and EPAMW01-0412-10 (lab ID should be 6521-14, not 6125-4). (b) The field duplicate pair for EPAMW01-0412 was above the 30% RPD limits for acetate and formate, note that the lab dup for this same sample was below 15% so this may be associated with true variation in the field samples. (c) The value for formate in sample PGDW20-0412 in the final summary spreadsheet should be 1.69 (not 1.63). (d) EPAMW02-0412-2 arrived broken. A sample designated for VOA analysis was used as a substitute as directed by the PI, Dr. Wilkin. VOA samples were preserved with TSP, low molecular weight acid samples with NaOH. This sample should be flagged J3 and J9. EPAMW02-0412-2 chromatogram appears questionable due to baseline issues.

Recommended Correction Action. (a) The lab IDs should be corrected as mentioned above in the final lab reports (note this does not affect final summary spreadsheet). (b) The J7 qualifiers on samples EPAMW02-0412-1, EPAMW02-0412-2 and EPAMW01-0412-10 should be removed from final summary spreadsheet, since these samples were not part of the field replicate pair that exceed the QAPP requirements. (d) Correct the final summary spreadsheet value for formate in sample PGDW20-0412 to read 1.69. (e) EPAMW02-0412-2 should be flagged with J3 and J9 as the original sample arrived broken and the VOA sample that was substituted wasn't preserved for low molecular weight acids per QAPP requirements. This same sample exhibited baseline problems during analysis. There is not an appropriate flag for baseline problems with a sample analysis. This should be addressed in the Pavillion report QA section Appendix B

Corrective Action Performed.

12. **Total Metals by ICP-MS.** Total lead and thorium were above the quantitation limits (QL) in the digestion blank. Lead was 0.274 µg/L and thorium was 0.076 µg/L. Samples with detected amounts that are less than 10x the blank concentration should be flagged LB.

Recommended Correction Action. Samples with detected amounts of lead and thorium concentrations that are less than 10x the concentrations in the digestion blanks should be flagged with LB.

13. **Microwave Digestion, Parameters for Total Metals.**

ADQ CHECKLIST

Number	ADQ Issue	Yes	No	NA	Comments
Sample Information					
1	Are samples uniquely identified and their identification correctly transcribed throughout the data package to the summary of results?	Yes*, except for low molecular weight acids.			Low MW Organic Acids: The lab IDs appear to be wrong in the lab report for PGDW05-0412 (lab ID should be 6511-04) and EPAMW01-0412-10 (lab ID should be 6521-14). These should be corrected in the final lab reports (does not affect final summary spreadsheet).
2	Does sample collection documentation indicate that samples were collected as described in the QAPP, and the schedule and volumes in the planning documentation?	Yes, with the exception of Field and Equipment Blanks that were not collected on every day of sampling.			All Analyses: A Field Blank, and in some cases an Equipment Blank, was not collected each day of analysis. This applies to all analytical suites to some extent. For example, only 3 equipment blanks were collected and the samples for DOC/DIC were collected on 7 different days. No Equipment Blank 3 was reported and no Field and Equipment Blanks were collected on 4/17, 4/19, and 4/20.
3	Does sample collection documentation indicate appropriate preservation?	Yes, except for GRO			GRO: Two samples were found to be above the pH value of 2 when they arrived at the laboratory: PGDW50-0412 (1204003-18) at pH of 7, and Equipment Blank 4 (1204003-